Energetics and dynamics of GaAs epitaxial growth via quantum wave packet studies

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Abstract

The dynamics of As_2 molecule incorporation into the flat Ga-terminated GaAs(100) surface is studied computationally. The time-dependent Schrödinger equation is solved on a two-dimensional potential energy surface obtained using density functional theory calculations. The probabilities of trapping and subsequent dissociation of the molecular As_2 bond are calculated as a function of beam translational energy and vibrational quantum number of As_2.

The molecular beam epitaxial (MBE) technique remains to be the major method to produce gallium arsenide, an important optoelectronic material. In this method, the GaAs surface which is kept at $\approx$ 600 K is irradiated by the gallium atomic beam and arsenic molecular beam composed mainly of As_2 and As_4 molecules [1–4]. For the Ga-terminated GaAs surface, the dissociative chemisorption of As_2 molecule leads to the growth of As layer. The probability of this process depends on the initial conditions of the molecular arsenic beam. This work aims to elucidate this dependence based on first principles calculations.

Several groups have studied the reaction mechanisms of GaAs MBE growth. Arthur [1], Foxon and Joyce [2], Tok *et al.* [3], and Ott *et al.* [4] have proposed various kinetic schemes based on the assumption of the molecular precursor-mediated reaction. The incorporation kinetics of Ga, As_2, and As_4 species into the GaAs(100) and (110) surfaces is modelled by a series of microscopic steps such as adsorption, desorption, chemisorption, and migration. These and another popular GaAs MBE growth modeling technique, the kinetic Monte-Carlo method [5–8], requires the detailed knowledge of energetics and microscopic rate constants of adsorption, desorption, and migration steps which is often is not available.

The chemisorption of As_2, As_4, and $GaAs_2$ clusters on a flat and step site of GaAs(100) surface was studied by Fukunishi et al. [9] using the Hartree-Fock method. The GaAs surface was modeled by a cluster and the total energy of the combined molecule-surface system was computed at several geometries. For As_2 molecule, the results indicate that the dissociative adsorption is more favourable at a step site than on a flat surface.

No *quantum wave packet* calculations have been reported so far for the incorporation dynamics of As_2 molecule into the GaAs(100) surface. The major difficulty lies in the absence of a reliable interaction potential for the Ga-As system, though several empirical potentials have been proposed over the years. [10,11] The quality of these potentials, which contain a number of fitting parameters, needs to be further tested.

In our study, the flat Ga-stabilized GaAs(100) surface is represented by the $Ga_8As_8H_{18}$ cluster similar to the one used in Ref. 9. The "excessive" dangling bonds of Ga and As atoms are saturated by H atoms. The geometry optimization is performed using the density

functional theory (DFT) [12] method with B3LYP hybrid functional. [13] The double-zeta LANL2DZ [14] basis set is used throughout the calculations. The calculations are performed using the Gaussian 94 program. [15] The As_2 molecule approaches the cluster and further chemically reacts with it. The two quantum molecular degrees of freedom in our model are Z - the distance between the As_2 center of mass and the central Ga atom of the surface cluster, and r, the As_2 internuclear coordinate (see Fig. 1). The conservation of C_{2v} symmetry is assumed in the simulations. After optimizing the geometry of the bare GaAs cluster, the chemical interaction with the approaching As_2 molecule is turned on and the resulting potential energy surface (PES) for the combined system is computed on a two-dimensional (Z,r) grid. The geometry of the surface cluster is held fixed at its previously optimized value which corresponds to the rigid surface approximation. The rectangular grid spans from 1.74 to 8.34 $\AA$ for the As_2 internuclear distance and from 0.16 to 9.16 $\AA$ for the translational coordinate Z. The size of the grid is 35 $\times$ 46. The neighbouring grid points are separated by 0.2 $\AA$ for each coordinate. The values of the potential in between the grid points are computed by using the bicubic interpolation method [16]. The resulting PES is shown for the chemically significant region in Fig. 2. The potential exhibits two minima and two saddle points. The global minimum (which is assigned zero of energy for the fitted potential) is located at r = 2.43 $\AA$ and Z = 2.17 $\AA$ and corresponds to the *molecular* adsorption of the As_2 molecule on the surface. The second minimum with an energy of 4032 cm^{-1} is located at r = 4.09 $\AA$ and Z = 1.56 $\AA$ and corresponds to the dissociation of the As_2 molecule into two As atoms on the surface. The effective locations of the saddle points in the incoming and dissociative channels are found by minimizing the potential over one of the coordinates while keeping track of the remaining one. The saddle point in the incoming channel occurs at r = 2.31 $\AA$, Z = 2.88 $\AA$ with an energy of 10644 cm^{-1}. The "vacuum" (i.e at large Z distances) energy of the As_2 molecule is 2776 cm^{-1}. This gives an activation energy, E_{act}, of 7868 cm^{-1}, which is close to 1 ev. The barrier in the dissociative coordinate r occurs at r = 3.36 $\AA$, Z = 1.73 $\AA$ and has an energy of 6122 cm^{-1}. We conclude that the molecular adsorption site is energetically more favourable than the dissociative one. This, however,

does not preclude the population of the latter site provided that the total initial energy of the beam is larger than the energy of the atomic chemisorption minimum.

The two-dimensional time-dependent Schrödinger equation (TDSE) for the As_2 - GaAs surface system is solved for the molecular Hamiltonian, $\hat{H}$, given by:

$$\hat{H}(Z,r) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial Z^2} + V(Z,r), \tag{1}$$

where $m = \frac{m_{As}}{2}$ is the reduced mass for the As_2 stretching coordinate r, $\mu = 2m_{Ar}$ is the appropriate mass for the translational coordinates Z, and $V(Z,r)$ is the As_2 - surface interaction potential.

A method based on the expansion of the wave function in a discrete variable representation (DVR) basis, has been used for solving the TDSE. [17–19] For both the Z and r coordinates we employ a plane wave original basis. [17] The DVR basis set is constructed from the original basis set using a standard procedure. [17–19] We have varied the number of DVR basis functions at each coordinate to ensure the convergence of the results. For the Z coordinate we determined that $N_Z = 751$ with $Z_{min} = 0.5\mathring{A}$ and $Z_{max} = 8\mathring{A}$ was adequate to obtain the converged results. Similarly, $N_r = 75$ with $r_{min} = 2\mathring{A}$ and $r_{max} = 5\mathring{A}$ was shown to be adequate for the internuclear coordinate r. A two dimensional DVR direct-product basis of order 56325 was used for wave function propagation.

The initial wave function is chosen as a product of a vibrational eigenfunction of the As_2 molecule, $\phi_v(r)$, and a Gaussian in translational coordinate Z.

$$\Psi(Z,r,t=0) = (2\pi\sigma^2)^{-\frac{1}{4}} exp(-\frac{(Z-Z_0)^2}{4\sigma^2} - ik_0 Z)\phi_v(r), \tag{2}$$

which is a wave packet centered on Z_0 with the average translational momentum in Z direction given by k_0 and the width of the coordinate (and momentum) distribution determined by σ. The average translational energy of the initial wave packet is:

$$< E_{tr} >= \hbar^2(k_0^2 + 0.25\sigma^2)/2\mu \tag{3}$$

Time evolution of the wave packet is achieved by expanding the propagator in a series of *modified* Chebyshev polynomials [20–23] which allows to include a large time step and

the absorbing potential into the original Chebyshev expansion. [24] The wave-packet was exponentially absorbed starting at $Z = 7.5$ $\AA$, in order to destroy the outgoing amplitude in the larger Z region before it could be unphysically reflected. At the present study we used 30000 Bessel functions for a total integration time of 3 ps.

Desorption was monitored by computing the outgoing probability flux through a dividing surface near the large Z boundary of the grid at a point before the absorbing boundary condition is applied. The large Z boundary of the grid is far away from the potential well of the adsorbate-surface complex so that the probability flux through the dividing surface corresponds to the scattering of the As_2 molecule off the surface. Let Z=S define the dividing surface, then the probability flux through this surface in the positive Z direction is given by

$$J(S,t) = \frac{\hbar}{\mu} Re \frac{1}{i} < \Psi^*(S,r,t) \mid [\frac{\partial}{\partial Z}\Psi(Z,r,t)]_{Z=S} >, \tag{4}$$

and the quantum desorption probability is defined as

$$P_d(t) = \int_0^t J(S,t')dt'. \tag{5}$$

We have used S = 7 $\AA$. The integral over time in Eq. 5 is evaluated numerically with the intermediate fluxes stored each 5 fs. This is accomplished by recomputing the time-dependent coefficients in modified Chebyshev expansion along with the values of the wave function and its derivative over the Z coordinate at Z=S only so that no storage of the full wave function and its derivative at each time step is required. We have also performed integration with a smaller time step of 0.5 fs and found the results similar to the 5 fs time step case. The reaction probability, P_r, is given by 1 - $P_d(t)$. P_r corresponds to the combined probabilily of sticking (molecular adsorption) and dissociation. The code was parallelized on 32 processors of SGI Origin2000 using high performance fortran. Almost linear scaling with the number of processors has been achieved.

The existence of the large activation barrier and the strongly bound molecular state significantly affects the dissociation dynamics by trapping As_2 near the GaAs surface and causing multiple reflections of the wave function. The trapped molecule can live for some

time as a resonant state, it can further dissociate into the atoms, or it can scatter back into the gas phase. Fig. 3 shows snapshots of $|\Psi|^2$ at four different times. The initial state has v = 0 and the initial translational energy equal to 10113.7 cm^{-1}. The average initial value of As-As stretching coordinate r is 2.18 $\AA$ and the average initial value of Z coordinate is 6.05 $\AA$. The wave packet is localized in both Z and r coordinates at t = 0. At t = 1 ps, the wave packet has significant amplitude both at large and small values of Z. The former corresponds to the nonreactive part of the wave packet which was reflected off the barrier in Z coordinate and is heading towards large Z values corresponding to desorption. The build up of the amplitude at small Z values corresponds to the molecular adsorption (sticking) of the As_2 molecule on the GaAs surface. Further dissociation of the As_2 molecule into individual As atoms is evident as there is some amplitude at larger r values. This process becomes even more prominent at t = 2 and 3 ps which shows gradual leakage of the amplitude into the area of large r values which corresponds to the dissociation of As_2 molecule. At the same time, the amplitude of the reflected part of the wave packet at larger values of Z diminishes meaning that almost no desorption is taking place anymore.

The reaction probabilities at t = 3 ps are shown in Fig. 4 as a function of the translational energy of the incoming wave packet for the ground and first two excited vibrational states of As_2. The activation energy in Z coordinate (E_{act} = 7868 cm^{-1}) is marked with the cross on the Z axis. In all the cases, there is a translational energy threshold below which the reaction does not occur. This reaction threshold is equal to $\approx$ 7300 cm^{-1} for the ground vibrational state which is lower than E_{act}. The reaction in the range of translational energies between 7300 and 7868 cm^{-1} occurs as a result of tunneling through the barrier into the molecular chemisorption well.

For the ground vibrational state, the reaction probability steadily increases with the initial translational energy, reaches a maximum value of around 17% at E_{tr} = 9779 cm^{-1} and decreases afterwards. For the excited vibrational states, the maximum of the reaction probability is observed at translational energies below E_{act} and the reaction probability slightly decreases with E_{tr} afterwards. We conclude that for E_{tr} below E_{act}, vibrations accelerate

dissociation. On the contrary, at translational energies above the E_{tr}, the vibrations promote scattering rather than dissociation.

Phenomenological explanation of the observed dependence is the following. At translational energies below E_{act}, the effective energy transfer from the low frequency (≈ 400 cm^{-1}) vibrational coordinate r to the translational coordinate Z facilitates tunneling through the barrier in the incoming Z-channel for the initially excited vibrational states. This increases the overall probability of As_2 dissociation for the excited vibrational states as compared to the ground vibrational state.

For the translational energies above E_{act}, the incoming wave function still feels the barrier and breaks into two pieces in its vicinity. One piece continues to move towards the surface into the molecular precursor state, while the second one is reflected back into the gas phase. The same picture holds for the wave function reflected off the repulsive wall of As_2 - surface potential at small Z. The r-coordinate is stretched in the vibrationally excited states comparing to the ground state (which has r = 2.18 $\AA$) and its value is close that of the entrance transition state (r = 2.31 $\AA$). As a result, the vibrationally excited wave function efficiently "penetrates" the Z-coordinate activation barrier both on the way in and out of the surface. After several reflections, the overall result for the vibrationally excited wave function is the increased probability of scattering at the expense of dissociation. The barrier in the dissociation channel occurs at a significantly larger r = 3.36 $\AA$ so that none of the initial vibrational wave functions have significant amplitude in this region.

In conclusion we have calculated, for the first time, the DFT-based PES describing the dissociation of As_2 molecule on the flat Ga-terminated GaAs(100) surface. Based on this PES, we have calculated the probabilities of As_2 sticking and dissociation as a function of beam translational and vibrational energy using quantum wave packet technique. The existence of the significant activation barrier and the strongly bound molecular chemisorption site indicates the importance of quantum effects in MBE growth of GaAs.

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FIGURE CAPTIONS

Fig. 1. The interaction of $Ga_8As_8H_{18}$ cluster, representing the flat Ga-stabilized GaAs surface, with the incoming As_2 molecule.

Fig. 2. The two-dimensional interaction potential describing the interaction of As_2 molecule with the rigid GaAs surface Saddle points are marked with crosses.

Fig. 3. Snapshots of modulus squared of quantum wave function for the ground vibrational state v = 0, and initial translational energy E_{tr} = 10113.7 cm^{-1} at t = 0, 1, 2, and 3 ps respectively.

Fig. 4. Combined probability of sticking and dissociation of As_2 molecule as a function of the initial translational energy for the ground and first two excited vibrational states.

Fig. 1

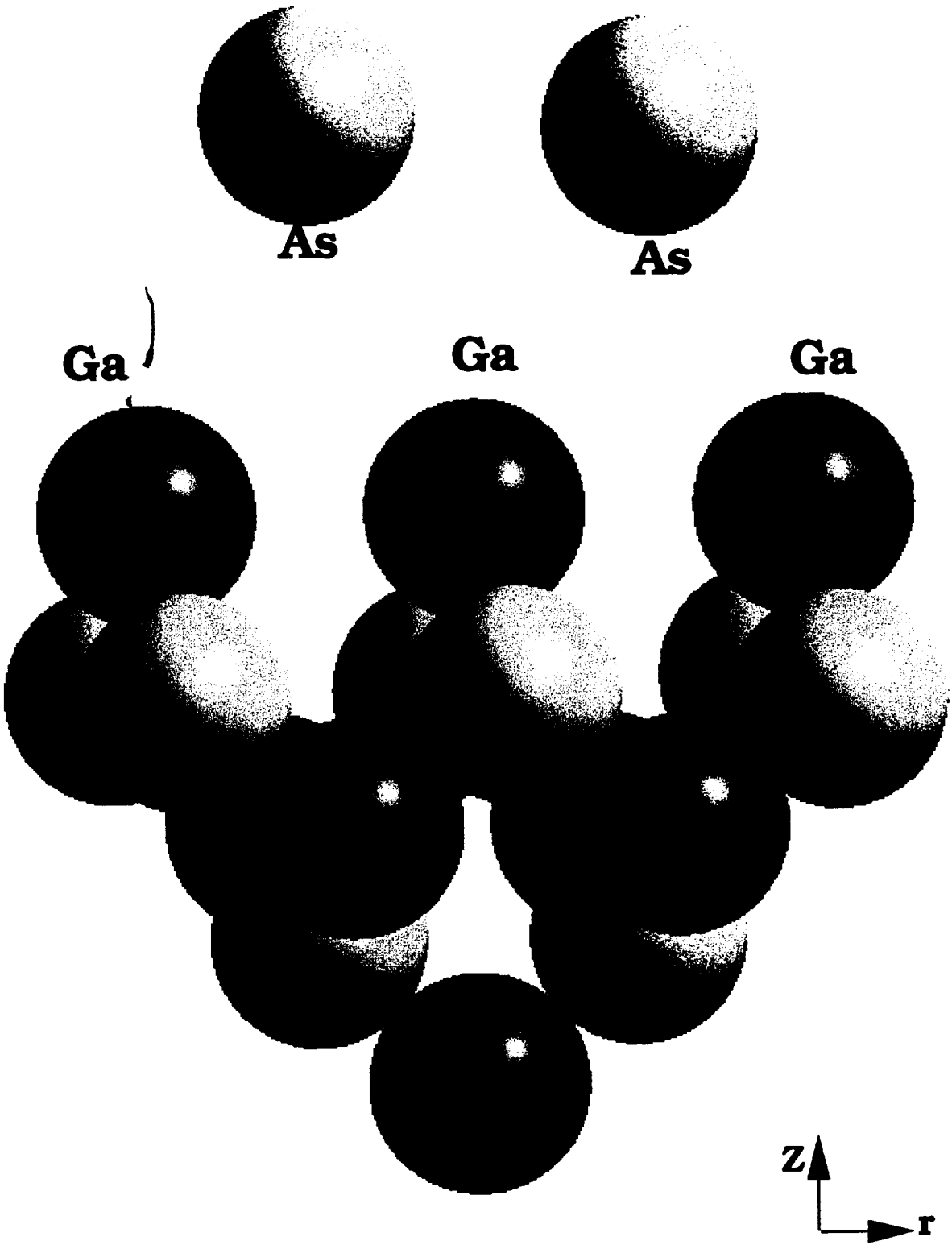
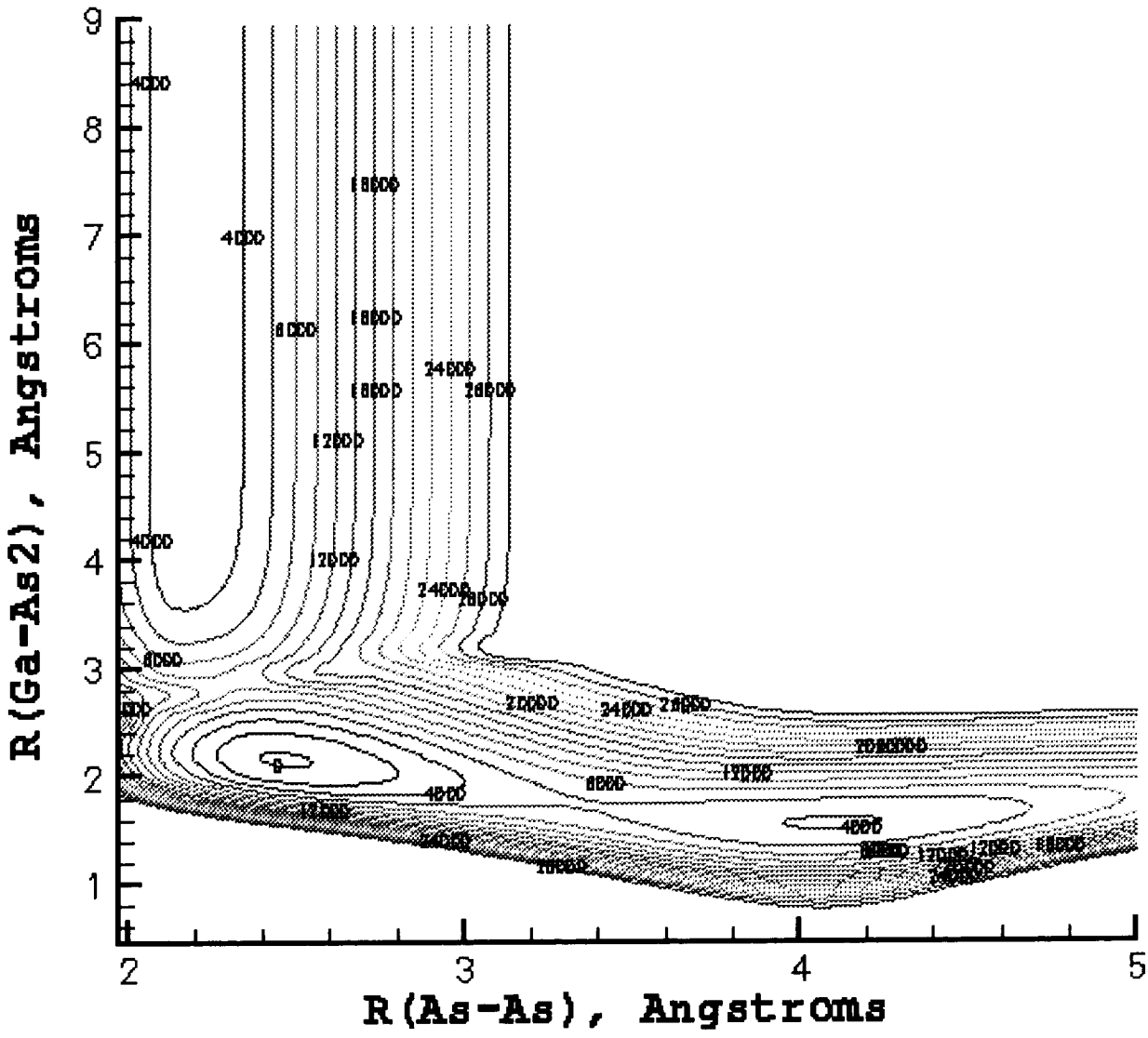
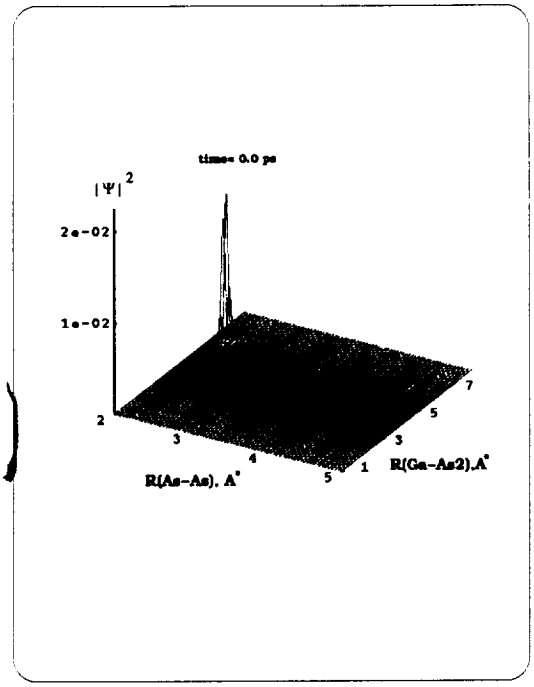


Fig. 2

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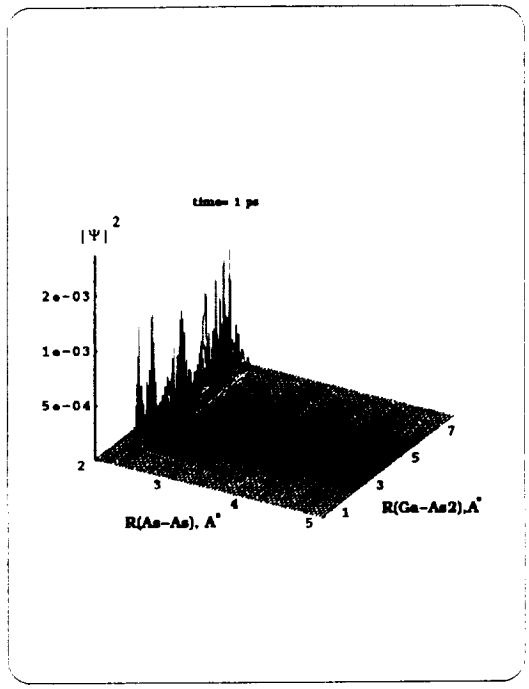
R(As-As), A°
R(Ga-As2),A°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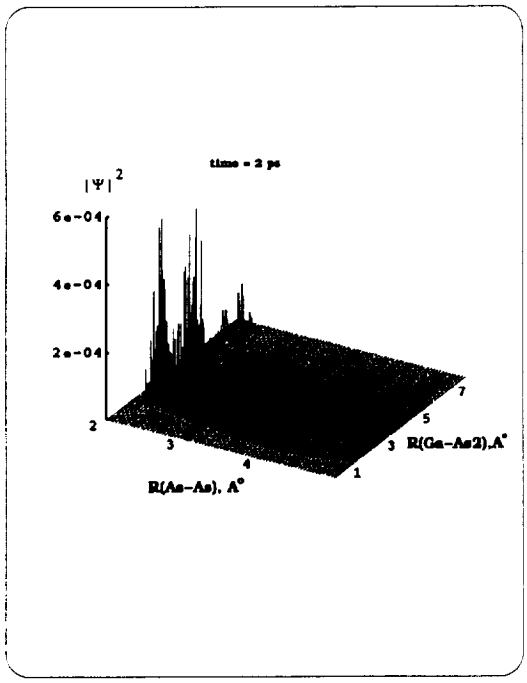
R(As-As), A°
R(Ga-As2),A°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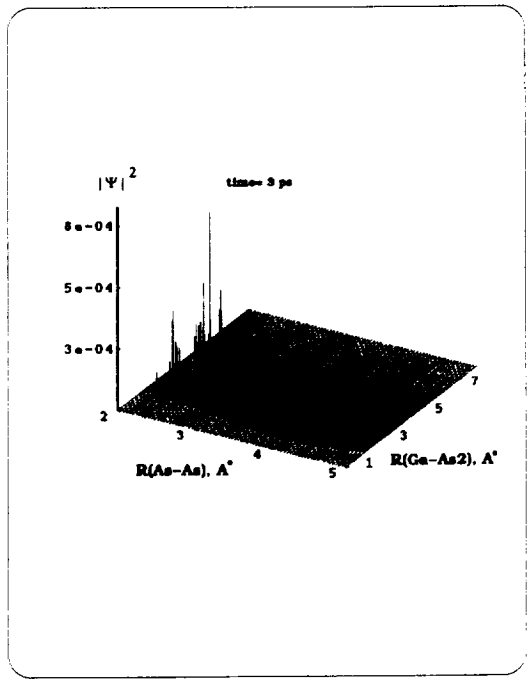
R(As-As), A°
R(Ga-As2),A°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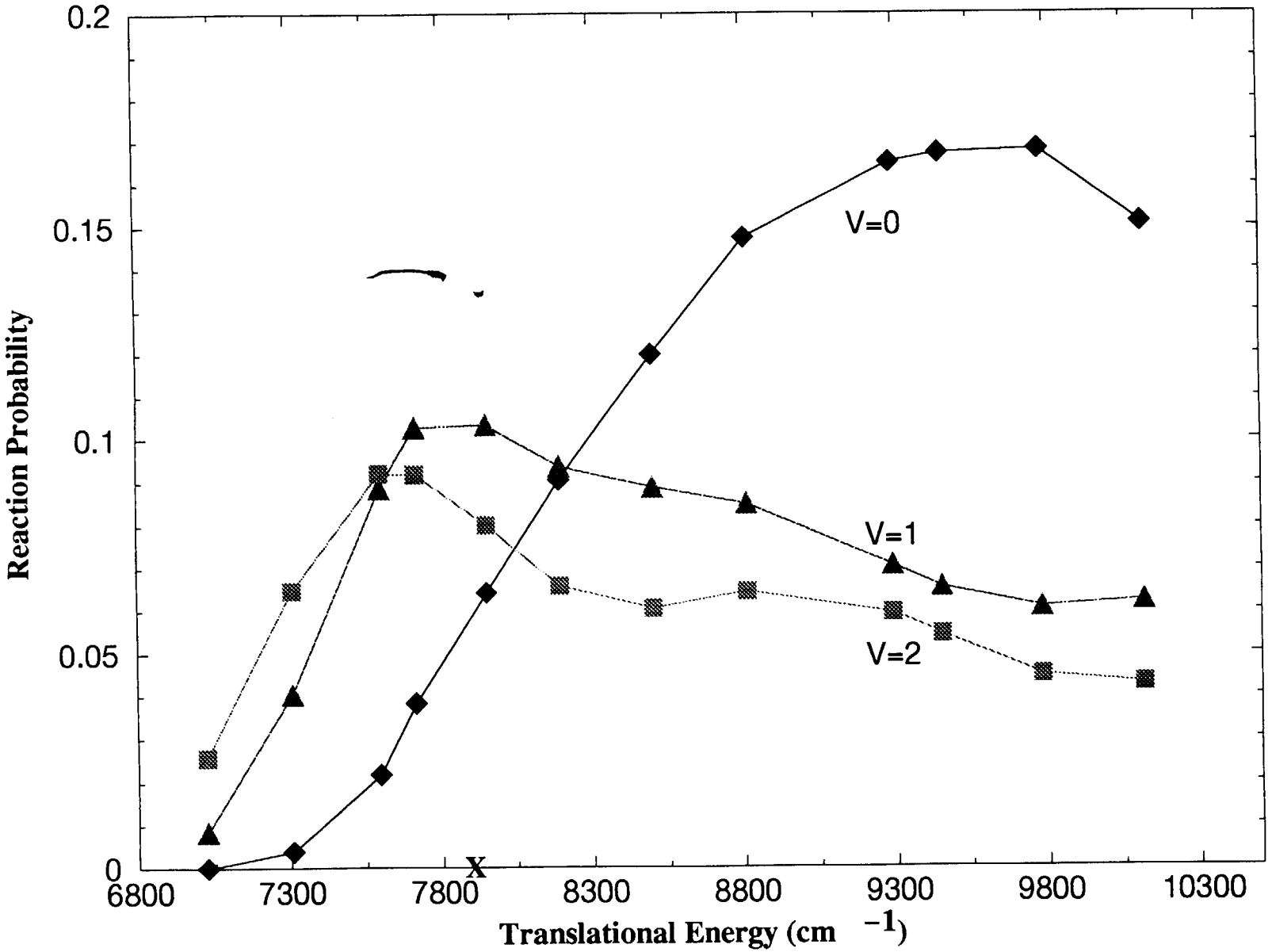
R(Ga-As2), A°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9300
9800
10300
Translational Energy (cm $^{-1}$)